

PREPARATION AND STUDY OF GROWTH STIMULATING ACTIVITY OF 1-PROPYL-4-(3'-AMINO-1', 2', 4'-TRIAZOLO-3'- THIOPROPINYL) PIPERIDIN-4-OL

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ABSTRACT. Results on the obtaining and the study of a plant growth stimulator based on 1-propyl-4-(3'-amino-1',2',4'-triazolo-3'-thiopropinyl) piperidin-4-ol are presented in the article. 1-propylpiperidin-4-on and 3-mercaptopropinyl-5-amin-1,2,4- triazolo were obtained with the basic parameters of the synthesis for synthesizing of 1-propyl-4-(3'-amino-1', 2', 4'-triazolo-3'-thiopropinyl) piperidin-4-ol. The structures of the obtained organic compounds were proved using IR spectroscopy and ¹H and ¹³C NMR spectrometry. The obtained 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropynyl)-piperidine-4-ol was tested for growth-stimulating activity on spring wheat grains compared with control (water) and has proved to be a domestic growth regulator «Akpinal-alpha» (KN-2).

Keywords: growth stimulators, organic compounds, IR spectroscopy, NMR spectrometry, growth stimulating activity, piperidine.

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INTRODUCTION

Increasing severe abiotic stresses, such as drought, salinity and extreme temperature changes, are part of the major impacts of climate change. These stresses led to the loss of soil organic matter and other forms of soil degradation, which adversely affects agricultural productivity [1]. Another important consequence of climate change and abiotic stress is an increase of plant infection with pathogens and pests [2]. Currently, intensive research is being undertaken to improve plant growth and tolerance to various abiotic stresses, as well as to protect plants from pathogens using growth stimulants that promote the growth of rhizobacteria, which have great potential for sustainable cultivation of crops [3-7].

Indigenous microbes, including endophytes, closely cooperate with each other and can serve as a link of important physiological processes, especially the production of nutrients and the suitability of plants to abiotic stresses [8-9]. Plants sown with growth stimulators modified with rhizobacteria produce more root hairs and take mineral and microelements more efficiently from the soil. The growth of several plants is enhanced by the treatment of growth promoter modified rhizobacteria, such as lentils (*Lens esculenta*) [10], peas (*Pisum sativum* L.) [11], cucumber (*Cucumis sativus*) [12], rice (*Oryza sativa*) [13] and soy (*Glycine max*) [6]. Growth stimulators modified with rhizobacteria also cause systemic tolerance to various abiotic stresses in plants, such as salinity, drought and heavy metals by changing plant physiology [14].

The beneficial properties of bacteria promoting plant growth include the ability to synthesize biologically active compounds such as plant growth stimulators [15-16], osmolites [8], antifungal compounds [17], and 1-aminocyclopropane-1-carboxylate enzyme deaminase [18]. The *Pseudomonas* strain was able to suppress soybean root disease caused by fungal pathogens [19] and showed counteracting activity against several fungal pathogens such as *Fusarium oxysporum* and *Rhizoctonia solani*. Induced systemic resistance of deciduous plants to pathogens caused by plant growth stimulating rhizobacteria was reported too [20]. In addition, some reports suggest that some plant growth promoting rhizobacteria cause systemic tolerance in plants through increased antioxidant reactions at the level of enzyme activity and metabolite accumulation [21-23]. The antioxidant defense system plays an important role in the adaptation of plants to saline stress, which makes it possible to purify reactive oxygen species (ROS) [24].

Variability in the efficacy of biological drugs is a concern when used under different conditions. Hostile environmental conditions are harmful for the microbiome associated with the root and for the effective functioning of

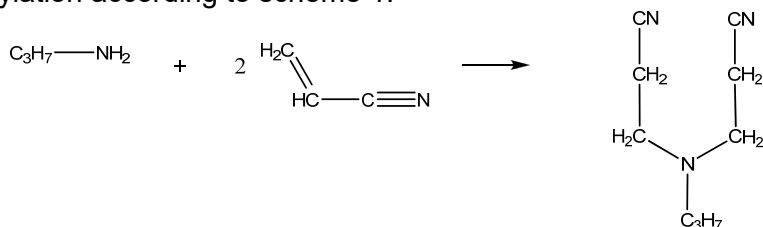
the injected rhizobacteria, that stimulate the growth of plant inoculants [17]. The effect of temperature on plant growth and on the ability of biological control of *Pseudomonas fluorescens* plant's growth stimulating rhizobacteria was observed in earlier studies [25]. In their study, these rhizobacteria suppressed *Fusarium* chickpea wilt at 30 °C, but not at 25 °C, in which the potential of the disease was high. It's interesting, that this suppression was associated with the production of extracellular metabolites that inhibit *F. oxysporum*, and the ability of rhizobacteria to stimulate plant growth, which was higher at 30 °C [17]. In this study, we obtained growth stimulator 1-propyl-4-(3'-amino-1',2',4'-triazolo-3'-thiopropinyl)piperidine-4-ol, studied their structural characteristics and evaluated the effect on the growth of stimulating activity of crops, namely grains of spring wheat.

The aim of this work is to obtain the growth stimulator 1-propyl-4-(3'-amino-1',2',4'-triazolo-3'-thiopropinyl)piperidine-4-ol and the study its growth-stimulating activity in relation to crops, namely grains of spring wheat.

RESULTS AND DISCUSSION

In the course of this work, acetylene alcohol 1-propyl-4-(3'-amino-1',2',4'-triazolo-3'-thiopropinyl)piperidine-4-ol was obtained in 4 stages and the optimal technological parameters of the reaction were selected to increase the yield of the target product.

Di-(2-cyanoethyl) propylamine was obtained by propyl amin cyanethylation according to scheme 1:



Scheme 1

To increase product yield of Di-(2-cyanoethyl)propylamine, optimal conditions were selected for carrying out reaction by changing such parameters as temperature and reaction time. As a result it was found that with increasing temperature product yield noticeably decreases and diminution in temperature till 10 °C also led to the yield decreases till 49%. The highest yield (54%) was achieved at room temperature (20 °C). As for reaction time, it was found that increasing of hours' number led to increase

of product yield too. When reaction continuance was 10 hours, the best yield was achieved and it was equal to 70%. The optimum parameters of reaction are presented in table 1. The structure and composition of the resulting compound were proved with a help of IR-spectroscopy.

Table 1. Parameters for obtaining of di-(2-cyanoethyl) propylamine

№	t, [°C]	Time,[h]	Yield,[%]	t, [°C]	Time,[h]	Yield, %
1	10	4	49	20	4	54
2	20	4	54	20	6	59
3	30	4	46	20	8	64
4	40	4	43	20	10	70

The presence of the characteristic functional groups of di-(2-cyanoethyl)propylamine was proved by IR-spectroscopy (Figure 1). There are absorption bands at 2248 cm^{-1} , which is characteristic for nitrile group, and adsorption bands at 2963 , 2874 , 2828 cm^{-1} , which is characteristic for the stretching vibrations of methyl, methylene groups were showed in the di-(2-cyanoethyl) propylamine IR-spectra.

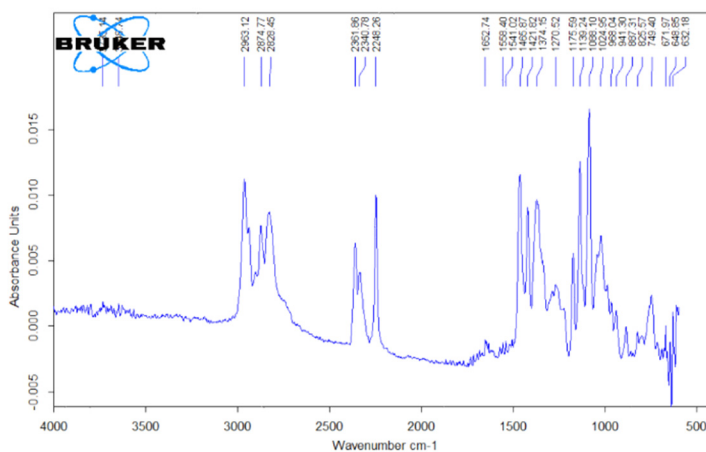
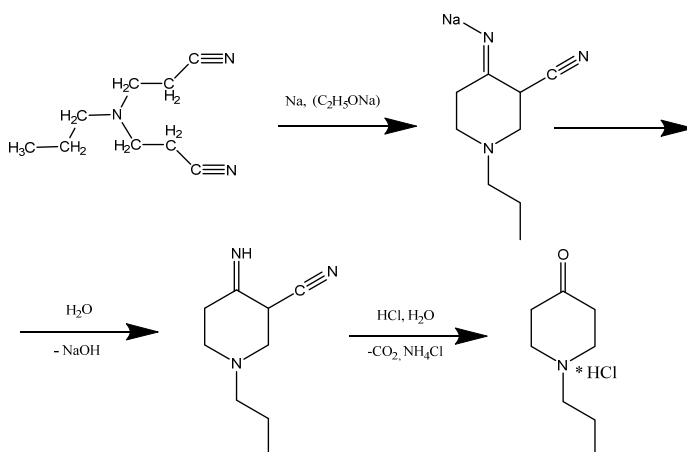


Figure 1. di-(2-cyanoethyl) propylamine IR-spectrum

Di-(2-cyanoethyl)propylamine obtained in the first stage was cyclized to 1-propylpiperidin-4-one (scheme 2) using a method similar to the one reported for the preparation of 1-methylpiperidine-4-one [27]:



Scheme 2

The cyclization reaction took place at 105°C in the medium of anhydrous toluene with an excess of metallic sodium. The reaction mixture was kept for 10 hours. The cyclization product was obtained in 41% yield.

In figure 2 is presented the IR spectrum of 1-propylpiperidin-4-one, which displays absorption bands, that were observed at 1638 cm^{-1} , corresponding to the stretching vibration of the ketone group, and absorption bands observed at 2959 , 2934 , 2873 cm^{-1} , which are characteristic for the stretching vibrations of methyl, methylene groups.

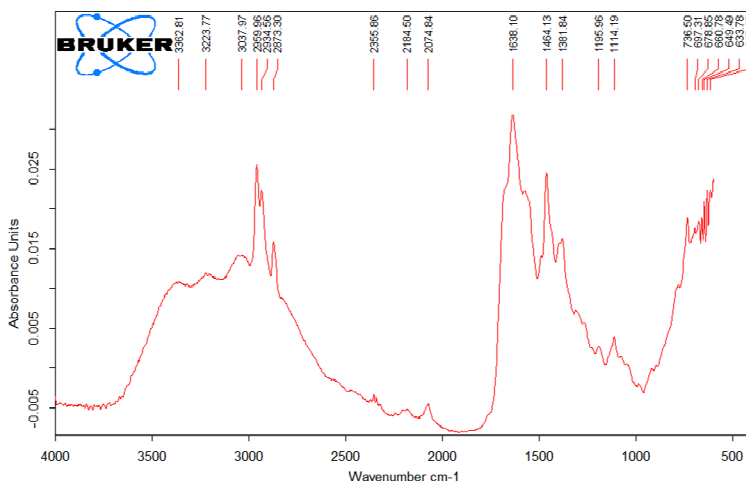
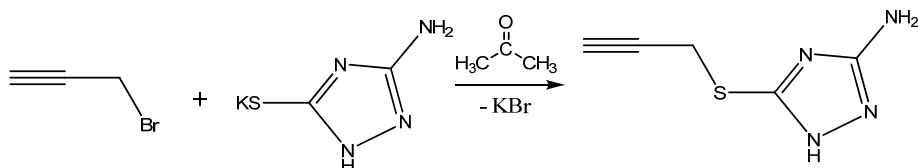


Figure 2. 1-propylpiperidin-4-one IR-spectrum

3-Mercaptopropinyl-5-amino-1,2,4-triazole was obtained by propargylation of potassium 1,2,4-triazolo-3-amino-5-sulfide with propargyl bromide in benzene as shown in scheme 3.



Scheme 3

Series of syntheses was carried out to optimize and increase the yield of the target propargylated triazole.

The reaction of propargylation with propargyl bromide of 1,2,4-triazolo-3-amino-5-potassium sulfide in ethanol was carried out for 8 hours at 75 °C, the product yield was 56%.

When interacting of 1,2,4-triazolo-3-amino-5-potassium sulfide with propargyl alcohol under similar conditions, the yield was 28% of the theoretical.

During the propargylation reaction with propargyl bromide of 1,2,4-triazolo-3-amino-5-potassium sulfide in benzene at 9-hour exposure to a temperature in range of 74 – 77 °C, a yield of 61% was achieved. And the interaction with propargyl alcohol, under the same conditions, led to a yield of 34% of the theoretical. The propargylation with propargyl bromide of 1,2,4-triazolo-3-amino-5-potassium sulfide in acetone with heating for 10 hours at 50 – 53 °C, yielded the product in 72%. When combining 1,2,4-triazolo-3-amino-5-potassium sulfide with propargyl alcohol for 10 hours in acetone at 50 – 53 °C the yield was 41%. In diethyl ether at 29 – 34 °C propargylation with propargyl bromide of 1,2,4-triazolo-3-amino-5-potassium sulfide within 11 hours of conversion of the target product, yield was 58 %. And during the interaction of 1,2,4-triazolo-3-amino-5-potassium sulfide with propargyl alcohol in diethyl ether under the same conditions 3-mercaptopropinyl-5-amino-1,2,4-triazolo was formed, and its yield was 37%. The main parameters of these methods are summarized in table 2.

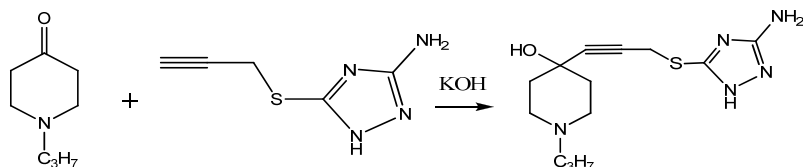
The structure of 3-mercaptopropinyl-5-amino-1,2,4-triazolo was confirmed by NMR spectroscopy (¹H and ¹³C). The ¹³C NMR spectrum is characterized by the presence of signals at 19.71 ppm, corresponding to the carbon of the methylene group of the propargyl substituent, signals at 73.89, 81.16 ppm are correlated with the acetylene carbon signals, and the signal at 154.91 ppm is correlated with the carbon in the fifth position of the triazole ring and a signal situated at 158.18 ppm is correlated with the carbon situated in the third position of the triazole ring.

Table 2. Reaction conditions applied in the preparation of 3-amino-5-thiopropynyl-1,2,4-triazole

№	Propargylating agent	Solvent	Temperature, °C	Time, h	Yield %
1	Bromide propargyl	Ethanol	75	8	56
	Propargyl alcohol		78	9	28
2	Bromide propargyl	Benzene	76	9	61
	Propargyl alcohol		80	8	34
3	Bromide propargyl	Acetone	52	10	72
	Propargyl alcohol		53	9	41
4	Bromide propargyl	Diethyl ether	29	11	58
	Propargyl alcohol		30	12	37

The ^1H NMR spectrum contains signal in the region at 0.1 ppm, corresponding to the hydrogen atom at the C-9 acetylene group. Signal at 3.73 ppm corresponds to the hydrogens of methylene group of the propargyl substituent. Hydrogen atoms under the amine substituent N-10 are prescribed as a broad signal at 6.09 ppm. Hydrogen at N-1 in the ^1H NMR spectrum is not prescribed according to substitution on D of the solvent.

1-Propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropynyl)-piperidin-4-ol was obtained by the reaction between 1-propylpiperidin-4-one and 3-mercaptopropynyl-5-amino-1,2,4-triazole (scheme 4):



Scheme 4

Series of reactions was carried out in different solvents and different ratio caustic potassium for selection of optimal conditions of the addition 3-amino-5-thiopropynyl-1,2,4-triazole to the 1-propylpiperidin-4-one (Table 3).

Table 3. Parameters of obtaining of 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropynyl) - piperidin-4-ol

№	Solvent	Ppm : KOH	Yield, %
1	Diethyl ether	1:3	59
		1:5	70
		1:10	76
2	Ethanol	1:3	48
		1:5	59
		1:10	68

At fivefold excess of caustic potassium in diethyl ether similar yields were obtained as at the interaction in the medium of diethyl ether with a tenfold excess (yield is 70% and 76%, respectively). With a decrease in amount of caustic potassium till threefold excess, the yield decreased till 59%. The replacement of the solvent to the ethanol, at the other equal conditions, adducted to the yield decrease on the average of 10%, from which was drawn a conclusion, that the optimal conditions were achieved when carrying out the reaction in diethyl ether with a tenfold excess of caustic potassium (Table 3).

The structure 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl) - piperidin-4-ol was confirmed by NMR-spectroscopy (H^1 and C^{13}). 1H NMR spectrum of compound of is characterized by the presence of three multiplet signals situated at 0.84-0.86, 1.65-1.67 and 2.91-2.93 ppm, corresponding to protons of the N-propyl substituent of piperidine ring H-9, H-8 and H-7, respectively. H-3,4 and H-2,6 Piperidine protons were resonated with the multiplets at 2.01-2.01 and 2.42-2.50 ppm., respectively. H-13 proton, which is located between sulfur atom and acetylenic fragment, was resonated with the singlet at 4.31 ppm. Amino group protons H-20 of the heterocyclic fragment were manifested by broad singlet at 5.11 ppm.

In the ^{13}C NMR spectrum there is a signal at 14.16 ppm, appropriate to the methyl carbon C-9 of the piperidine ring's propyl substituent. The peaks will correspond to the methylene substituent C-8, C-7 of propyl radical in area 22.75 and 24.55 ppm. Signal at 23.45 ppm. corresponds to the methylene group C-13 of the propyl radical. Methylene carbons C-2, C-6 of the piperidin ring prescribes in area 26.47 ppm., and C-3, C-5 at 29.76 ppm. Quaternary carbon C-10 prescribes at 29.42 ppm. Signals at 31.99 and 32.28 ppm. correlate with acetylene carbons C-11 and C-12. Signal at 125.16 ppm. corresponds to the C-15 carbon atom of triazol ring, respectively carbon's atom C-18 prescribes at 135.29 ppm.

The obtained 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl)-piperidin-4-ol was tested for growth-stimulating activity on spring wheat grains compared with control (water) and has proved to be a domestic growth regulator «Akpinol-alpha» (KN-2).

For exploring growth-stimulating activity of obtained compound there were prepared hydrochloride solutions of 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl)-piperidin-4-ol at the following concentrations: 0.01%, 0.001%, 0.0001% and model solutions of KN-2 in similar concentration.

Also, samples were selected for 100 wheat grains, which preliminary were soaked during 2 hours in obtained solutions. Then grains were placed into Petri dishes for intergrowth (Figure 3). The experiment was conducted for 5 days, during which the length of the roots and shoots of germinated grains was measured.

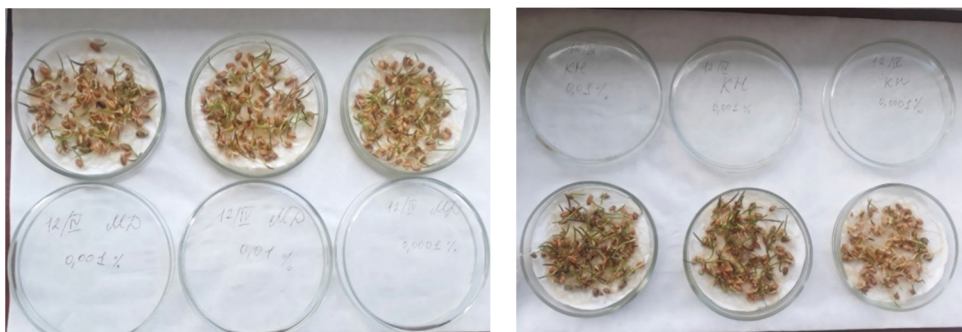


Figure 3. Germination of spring wheat grains in the presence of 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl)- piperidin-4-ol (left) and KN-2 (right) in solution concentrations: 0.01%, 0.001%, 0.0001%

Results of growth-stimulating activity of 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl) - piperidin-4-ol are presented in table 4.

Table 4. The effect of the 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl) - piperidin-4-ol plant growth regulators on wheat germination

Growth-stimulator	Conc., %	Root length, mm	Shoot length, mm
Control (water)	-	43, 36, 25	36
1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl)-piperidin-4-ol	0.01	22, 26, 15	21
	0.001	43, 34, 23	36
	0.0001	46, 30, 28	29
Ethanol (KN-2)	0.001	36, 28, 27	27

The results showed that 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl)-piperidin-4-ol have growth-stimulating activity and the parameters exceed the model drug. The dependence of activity on the concentration of the drugs was also observed. At the concentration increase (0,01%) there appears inhibitory effect of the drug and deceleration of wheat growth is observed. Decrease of the concentration till 0,0001% markedly leads to increase wheat's growth and accordingly, growth stimulating activity.

In this way, it is found out, that the maximum germination of wheat is observed at the 0,0001% concentration of 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl) - piperidin-4-ol.

CONCLUSIONS

1-propyl-4-(3'-amino-1',2',4'-triazolo-3'-thiopropinyl)-piperidin-4-ol, which shows the properties of plant growth regulator was obtained. 1-propylpiperidine-4-on and 3-mercaptopropyl-5-amino-1,2,4-triazolo were synthesized to obtain this compound in compliance with the basic parameters of the synthesis.

The structures of the obtained organic compounds were confirmed by IR spectroscopy, ^1H and ^{13}C NMR spectrometry.

The obtained compound is 1-propyl-4-(3'-amino-1',2',4'-triazolo-3'-thiopropinyl)-piperidin-4-ol and it was tested for growth-stimulating activity on spring wheat seeds by seed germination method. From the obtained preliminary results, it was concluded that the maximum germination of wheat was observed when the concentration of a solution of 1-propyl-4-(3'-amino-1',2',4'-triazolo-3'-thiopropinyl)-piperidin-4-ol is equal to 0.0001%.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on the JNM-ECA Jeol400 spectrometer (frequency is equal to 399.78 and 100.53 MHz, respectively) using CDCl_3 solvent. Chemical shifts are measured toward to the signals of residual protons or carbon atoms of deuterated chloroform.

IR spectra of the obtained compounds were recorded on the Infra-Lum-FT 02 spectrometer (LUMEX, Russia) in the frequency range of 4200-400 cm^{-1} (in a thin layer for liquid compounds).

1. Propylamine cyanethylation

A 69.4 g (1.18 mol) of distilled propylamine was added dropwise under stirring to a 106 g (2 mol) of acrylonitrile. Reaction mass stirred at room temperature for 10 hours. The reaction mass was dispersed in a vacuum of a water-jet and oil pumps.

Bis(2-cyanethyl)propylamine Yield 105 g (70%). bp 158-160 °C (3-4 mmHg); $n_D^{20} = 1.4627$. IR (KBr, cm^{-1}): 2248 (CN), 2963, 2874, 2828 (CH_3 , CH_2).

2. Synthesis of 1-propylpiperidin-4-one

A solution of bis(2-cyanethyl)propylamin (10 g, 0.06 mol) in 20 mL of toluene with sodium (0.83, 0.03 mol) was stirred under reflux in anhydrous toluene at 100-105 °C for 10 hours. After all of the sodium has completely reacted, 20 ml of hydrochloric acid solution are added dropwise to pH = 1. After separation, the aqueous layer was cooled, basified to pH = 10. The separated organic layer was repeatedly extracted with ether. The ether layer was dried over calcined potash, the ether was distilled off, and the residue was distilled in a vacuum of an oil pump.

1-Propylpiperidin-4-one Yield 4.1 g (41%). bp 158-160 °C (3-4 mmHg); $n_D^{20} = 1.4566$. IR (KBr, cm^{-1}): 1638 (C=O), 2959, 2934, 2873 (CH_3 , CH_2)

3 Synthesis of 3-mercaptopropinyl-5-amino-1,2,4-triazole

16.25 g (0.11 mol) of propargyl bromide in 20 ml of acetone were slowly added dropwise to a solution of 14.2 g (0.1 mol) of triazole in 50 ml of acetone heated to 50 °C. The next day, the reaction mass was filtered and the solvent was distilled on a rotary evaporator.

3-mercaptopropinyl-5-amino-1,2,4-triazole Yield 3.16 g (77%). mp 152 °C. ^1H NMR (400 MHz, DMSO- D_6) δ 7.52 (s, 1H), 6.11 (s, 1H), 3.73 (d, $J = 12.2$ Hz, 2H), 2.96 (d, $J = 4.5$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO- D_6) δ 157.90 (s), 154.58 (s), 80.67 (d, $J = 23.6$ Hz), 73.59 (d, $J = 20.1$ Hz), 19.46 (s).

4 Synthesis of 1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl)-piperidin-4-ol by the Favorsky reaction

A mixture of 1.1 g (0.009 mol) of 1-propylpiperidin-4-one (2), 2.24 g (0.04 mol) of technical KOH and 200 mL of diethyl ether was stirred under heating (not more than 30 °C) for 1-2 hours. Next, 1.2 g (0.008 mol) of propargylated triazole in 20 ml of ether was added dropwise at room temperature. After stirring for 2 hours, cold water was added to the reaction mixture, and the separated organic layer was extracted with ether. The ether layer was dried over calcined potash. The ether was distilled off, and the residue was washed repeatedly with acetonitrile until a precipitate formed.

1-propyl-4-(3'-amino-1'2'4'-triazolo-3'-thiopropinyl)-piperidin-4-ol Yield 1.75 g (76%). mp 185 °C. ^1H NMR (400 MHz, CDCl_3): δ 5.11 (s, 1H), 4.38 (s, $J = 16.2$ Hz, 1H), 2.82 (d, $J = 58.0$ Hz, 3H), 2.60 – 2.18 (m, 4H), 2.02 (s, 2H), 1.66 (s, 1H), 1.23 (s, 10H), 0.85 (d, $J = 7.1$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.10 (s), 124.93 – 124.73 (m), 31.97 (s), 29.67 (d, $J = 11.0$ Hz), 29.33 (s), 26.18 (s), 23.19 (s), 22.41 (s), 14.03 (s).

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